

Nitrogen- and phosphorus-co-doped carbons with tunable enhanced surface areas promoted by the doping additives†

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1-Butyl-3-methyl-pyridinium-dicyanamide (BMP-dca) is carbonised with tetra-alkyl-phosphonium-bromide additives yielding nitrogen- and phosphorus-co-doped carbons with enhanced BET surface areas promoted by the additives.

Heteroatom doping of carbon materials is an emerging field of materials science. Nitrogen is by far the most prominent doping candidate and numerous examples with versatile applications, *e.g.* in electrochemistry, are known.^{1–22} Although other heteroatoms are of thriving interest, synthetic pathways towards boron-,^{23–26} sulphur-^{27–35} and phosphorus-doped^{36–38} carbons are still rare. As especially bigger atoms like S or P have most preferable effects on the polarisability of the carbon materials and thus on their performance in electrochemical applications,^{31–36} new synthesis routes are inevitable. IL based syntheses of carbon materials have been established in manifold ways in recent years of research.^{1–7,21–23,39–48} Especially liquid salts with dicyanamide anions are a powerful precursor for N-doped carbons,^{1–7} and for advanced co-doping with S.²⁷ Herein we present a modified IL route using phosphonium additives, paving the way towards P- and N-co-doped carbons – a class of materials only rarely reported in the literature so far.³⁶

BMP-dca with 40 mol% of tetrabutyl-phosphonium-bromide (TBuPBr) as a phosphorus source was therefore carbonised at 1000 °C in a constant flow of inert gas (see ESI† for details). The black solid product is a carbonaceous material exhibiting a local graphitic order that is limited in its extension. This can be derived from the powder X-ray diffraction (PXRD) patterns showing broadened, but intense, (002) and (100) reflexes typical for a stacking motif in turbostratic-like carbons (compare Fig. S1, ESI†). The black product was also characterised by

means of elemental combustion analysis (EA) and inductively coupled plasma optical emission spectrometry (ICP-OES) to determine the degree of heteroatom-doping: 4.1 wt% of N-doping (EA) and 5.7 wt% of P-doping (ICP-OES) are revealed. The material is thus successfully dually doped; especially the remarkably high degree of P-doping compared to other approaches^{36–38} is noteworthy and points out the advantages of the method. To also prove the homogeneity of the material, elemental mapping based on energy dispersive X-ray spectroscopy (EDX) and wavelength dispersive X-ray spectroscopy (WDX) was performed. The data are provided in the ESI† (Fig. S2–S5, ESI†), showing clearly that the dopants are spread homogeneously throughout the material. Significant local concentration maxima cannot be found.

The binding environments of both N and P could be elucidated by X-ray photoelectron spectroscopy (XPS), and the detailed N1s and P2p scans are depicted in Fig. 1. The results for nitrogen are as expected according to our previous studies:^{1,2,27,46} three deconvoluted contributions appear at 398.13 eV, 400.88 eV and 402.80 eV that can be assigned to pyridinic and pyrrolic nitrogen species, quaternary graphitic nitrogen and minor oxidised nitrogen binding motifs (due to oxidative processes on the surface of the materials), respectively.^{16,34,49,50} The N doping thus occurs with N atoms firmly bound to the carbon backbone. To clearly assign the P2p XPS scan to certain chemical environments is however more difficult.

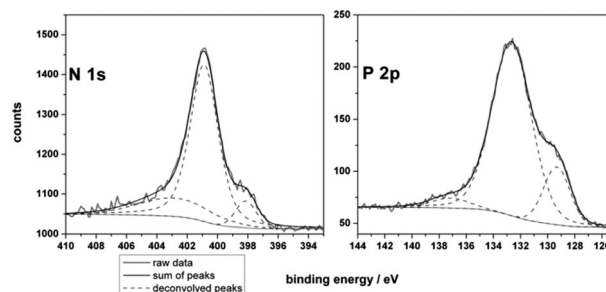


Fig. 1 Deconvoluted XPS scans of the N1s and P2p orbitals of the material.

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Three deconvolved contributions appear at 129.33 eV, 132.66 eV and 137.15 eV. The value of ~ 137 eV has been observed for phosphorus in high oxidation states,⁵¹ thus referring to surface oxidised P species. The two more dominant contributions are controversially discussed,^{37,51–53} but the most comprehensive explanation is the contribution at 132.66 eV attributed to P–C-binding motifs.^{37,51} In this range of binding energies, P atoms neighbouring N have also been reported,⁵¹ which is also comprehensive. The binding energy of 129.33 eV derives from P–P binding sites.⁵¹ The assignment of the P2p XPS scan is thus not totally clear, but considering both the data reported in the literature and the chemical circumstances of our synthetic approach, the explanation of P firmly bound to the carbon backbone is the most comprehensive. The XPS data also reveal the changes in the chemical environments of the dopants during the formation of the material. Nitrogen atoms are already part of aromatic units in the precursor, or are easily incorporated by triazine formation. Phosphorus atoms do not appear in any aromatic environment in the precursor system. However, P atoms are nevertheless already bound to carbon atoms in the phosphonium salts used, easing their incorporation into the forming carbon backbone.

The nitrogen sorption isotherm of the P/N-doped material (see Fig. 2) surprisingly showed that the co-doped carbon does exhibit an enhanced BET surface area of ~ 283 m² g^{−1}. As purely N-doped carbon derived from BMP-dca without additives is just a bulk material, this alteration must be due to the structure directing effect of the phosphorus source. We focused on this phenomenon more closely by investigating the effect of different additives. Interestingly, tetra-alkyl-phosphonium-halides with nitrile groups ((4-cyanobenzyl)-triphenyl-phosphonium-chloride [CN-add-1] and cyanomethyl-triphenyl-phosphonium-chloride [CN-add-2]) used as additives (40 mol% in BMP-dca, 1000 °C under inert gas flow) did yield P/N-codoped carbons (N: 5.1 wt% (both additives)/P: 3.5 wt% (CN-add-1) and 6.9 wt% (CN-add-2)), but the materials did not exhibit any enhancement of the BET surface area. The nitrile groups surely promote an intensified chemical reactivity by triazine formation between the BMP-dca and the additive at an earlier stage of the reaction. In contrast, different nitrile free phosphonium additives show the structure directing properties, which we investigated using TBusPBr, tetra-ethyl-phosphonium-bromide (TETPBr) and tetra-phenyl-phosphonium-bromide (TPHPBr) as additives at different concentrations. All nitrogen sorption isotherms are

Table 1 BET surface areas of BMP-derived P/N-codoped carbons using different phosphorus sources at various concentrations

	TETPBr	TBusPBr	TPHPBr
10 mol%	0.2 m ² g ^{−1}	2 m ² g ^{−1}	1.5 m ² g ^{−1}
20 mol%	17 m ² g ^{−1}	41 m ² g ^{−1}	10 m ² g ^{−1}
30 mol%	32 m ² g ^{−1}	137 m ² g ^{−1}	146 m ² g ^{−1}
40 mol%	80 m ² g ^{−1}	283 m ² g ^{−1}	253 m ² g ^{−1}

shown in Fig. 2, the respective BET surface areas are summed up in Table 1.

The values reveal a clear tendency of tetra-alkyl-phosphonium additives to promote the enhancement of the BET surface area in IL-derived carbons. Both the properties of the alkyl chains and the concentration of the additives determine the achieved surface areas, indicating a templating effect of the phosphonium salts. Both external surfaces and mesoporosity contribute to the measured surface areas, which can be estimated from the shapes of the measured isotherms. Transmission electron micrographs (TEM) support this idea, showing the sponge-like structures of the two materials with the highest surface areas, synthesised using TBusPBr- and TPHPBr-concentrations of 40 mol% (see Fig. S6, ESI†).

Although the intrinsic increase of the surface area is highly interesting, from an application directed point of view it should be further enhanced. We were able to achieve this using Ludox[®] silica nanoparticles as a hard template during the synthetic procedure. Removal of the template yields a P/N-co-doped carbon – P: 4.8 wt% (ICP-OES)/N: 2.8 wt% (EA) – with an open mesoporous structure. The morphology can be seen in the micrographs in Fig. 3 and the nitrogen sorption isotherm is depicted in Fig. S7 (ESI†), showing a typical hysteresis for mesoporous materials with disordered pore structures and exhibiting a BET surface area of 832 m² g^{−1}.

It can be concluded that this work presents a novel pathway towards multiply-doped carbons containing phosphorus. Especially the intrinsically increased surface areas promoted by the applied phosphonium additives make the material highly interesting, while additional mesoporosity can be easily induced by hard templating. Furthermore, the possibility of finely modifying cheap commercial carbons with such an advanced material – which is envisaged – makes the IL-derived P/N-co-doped carbon a promising candidate for electrocatalytic or other applications.

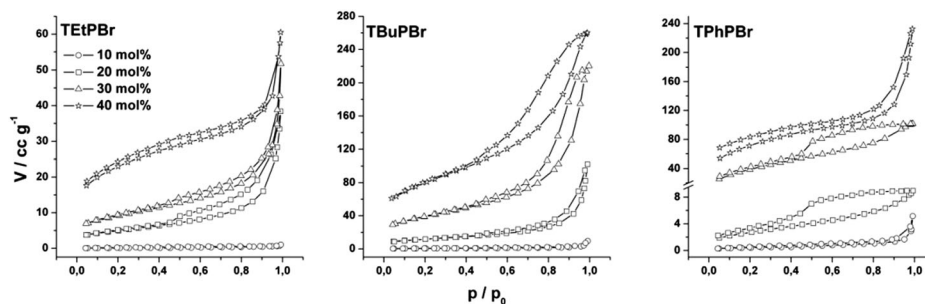


Fig. 2 Nitrogen sorption isotherms of BMP-dca derived carbon using different additives at different concentrations.

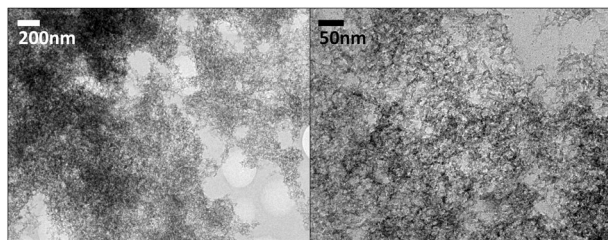


Fig. 3 TEM micrographs of the Ludox[®] templated sample.

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